NOVEL

CHROMIUM-FREE SURFACE PRETREATMENT PROCESS FOR CORROSION INHIBITION

by

Francis L. Keohan, Hege J. Lizarralde, Peter Phillips and Anthony Arvanites
Cape Cod Research, Inc.
19 Research Road
East Falmouth, MA 02536
Phone: (508) 540-4400

I. Carl Handsy, Thomas M. Landy and Donald T. Ostberg
U.S. Army Tank-automotive and Armaments Command
Tank-Automotive Research, Development and Engineering Center
ATTN: AMSTA-TR-E/MATL/267
Warren, MI 48397-5000
E-mail: HYPERLINK mailto:landyt@cc.tacom.army.mil landyt@cc.tacom.army.mil
Phone: (810) 574-5954

ABSTRACT

The need to eliminate hazardous materials and processes from pre-bond surface treatments has increased industrial interest in mechanical abrasion for cleaning, deoxidizing and roughening metallic adherends. The surface treatments described in this study use simpler and less hazardous means than traditional chemical etching to prepare metals for structural bonding and coating. The overall approach involved surface abrasion with both medium pressure water and abrasives and abrasive-free ultra high pressure water followed by treatment with aqueous organosilane solutions and chromium-free, waterborne primers. Both abrasive and non-abrasive pretreatments yielded excellent maintenance of paint adhesion and corrosion resistance under salt spray and GM Spec 9540P cyclic corrosion test conditions. Control adhesive pretreatments included the the P2 etch and phosphoric acid anodizing. The initial strength and durability of bonds prepared by standard and experimental pretreatment methods using bare and clad aluminum alloys of the 2XXX, 5XXX and 7XXX series and several commercial epoxy-based adhesives were measured by the tensile lap shear, floating roller peel, and wedge opening tests. The approach yielded adhesive bonds whose initial strength and durability in hostile environments met or exceeded those attained for adherends prepared by the control pre-bond surface treatments.

KEYWORDS: pretreatment, water jetting, adhesives, paint, abrasion, organosilanes, corrosion

1.0 INTRODUCTION

The combination of mechanical abrasion and organosilane coatings has been used as an alternative to traditional prebond surface treatments such the sulfo-chrome etch and chromic acid anodization. The techniques reported to date generally involve dry abrasive blasting followed by silane deposition or manual sanding in the presence of hydrolyzed organosilanes. An extension of this approach that provides simpler waste management and potentially more effective adhesion promotion is high-pressure blasting with partially hydrolyzed silane coupling agent solution and abrasive. The method has been found to be effective for rapidly removing surface contaminants and metal oxides and replacing them with a primed layer containing silicate boundary layers. The Primer Activated Surface Treatment (PAST) process incorporates the passivation of metal surfaces by the combination of mechanical abrasion from hydrosanding and interaction with hydrolyzed organosilane priming agents. The freshly exposed metal can be considered an activator for organosilane deposition and condensation. It has been demonstrated that organosilane films over ferrous and non-ferrous metals can inhibit corrosion and promote strong adhesion of paint and commercial adhesives.

Additional waste minimization was realized by increasing the water blasting pressure and removing solid abrasives such as aluminum oxide from the blast stream. The non-abrasive PAST (NA-PAST) process passivates metal surfaces by combining abrasive-free, mechanical abrasion from ultra high pressure water jetting and interaction with hydrolyzed organosilanes. This report describes the paint removal, corrosion test results and adhesion performance of non-ferrous alloys prepared by the NA-PAST process.

The objective was to develop an effective, easily applicable surface treatment for aluminum and titanium alloys to replace currently used prepaint methods that rely on toxic and corrosive chemicals such as chromate conversion coatings. The approach was to explore alternative methods of metal deoxidation and stabilization through abrasive-free waterjet abrasion and application of an organosilane pretreatment.

The report below is but a small subset of the actual testing which occurred during the initial study of organosilane chemistry. Due to page constraints, only the results of accelerated corrosion testing are presented. Cape Cod Research also performed an in-depth study of the chemical reactions between organosilanes and native aluminum substrates as well as performing outdoor weathering, salt spray resistance and chip/abrasion resistance testing. The reader is welcome to contact the author for more information on these test results as well as for a current status of production-scale testing of the organosilane formulations at the National Defense Center for Environmental Excellence.

2.0 EXPERIMENTAL

2.1 Abrasive-Free NA-PAST Pretreatment Process

The NA-PAST process consists of four steps:

The degreased metal substrates are first deoxidized by ultra-high pressure (30-50 ksi) water blasting.

The deoxidized surfaces are treated with proprietary blends of hydrolyzed organosilanes in aqueous solution (note: the organosilane can be applied simultaneously during the hydrosanding by injecting concentrated solutions in the blast stream or it can be applied in diluted form after hydrosanding).

3) The organosilane passivation coating is dried at 93°C (200°F) for one hour.
4) A chromate-free, waterborne corrosion inhibiting adhesive primer is applied.

2.2 Organosilane Solution Formulation

Preliminary surface passivating agent formulations were prepared by dissolving commercially available organosilanes such as 3-glycidoxypropyltrimethoxysilane (GLYMO) and 3-mercaptopropyltrimethoxysilane (MPTMOS) in deionized water at a concentration of 1 percent on a weight basis. The solutions were stirred at ambient temperature for a period of 45 minutes to one hour before applying to deoxidized metal substrates. Various additives including organic dyes, surfactants, acids, and other organosilanes were used in these formulations to alter such properties as hydrolysis rate, surface wetting, surface film coloration for visual quality determination, and solution stability.

The organosilanes were chosen for their chemical compatibility with aluminum and titanium alloys as well as the components of typical corrosion-inhibiting primers. The degree of organosilane hydrolysis and aqueous solubility was controlled by formulation pH and by blending various organosilanes. The addition of organosilanes to water does not significantly change the viscosity but can have a dramatic effect on the surface wetting characteristics of the resulting solutions.

2.3 Preparation of Aluminum Panels for Laboratory Cyclic Corrosion Testing

Corrosion test panels were prepared by the NA-PAST process for cyclic corrosion analysis. Water pressures of 40,000-45,000 psi was used to prepare Al 2024-T3, 6061-T6, and 5086-H321 panels. The experimental corrosion-inhibiting primer for this evaluation was ACP-6, which was found to yield the best and most consistent results in continuous salt spray testing (ASTM B117) for samples prepared by the abrasive PAST process. Some of the NA-PAST-treated panels were primed with a commercial corrosion-inhibiting primer conforming to MIL-P-53022. Some of the primed panels were coated with a chemical agent resistant coating (CARC) topcoat conforming to MIL-C-46168 and some were not topcoated. These specimens and suitable controls (solvent degrease, alkaline clean, acid etch, desmut, Alodine®, MIL-P-53022) were tested in accordance with GM Spec 9540P, Method B and evaluated to ASTM D-1654, Procedure A.

3.0 Results of Corrosion Testing of Specimens Treated by NA-PAST Method

Coated corrosion test specimens (ten specimens per condition) prepared from Al 2024-T3, 5086-H32, and Al 6061-T6 alloys by the optimized NA-PAST/MPD/ACP-6 process and control pretreatments were tested for corrosion resistance under cyclic exposure (per GM Spec 9540P, Method B) and found to exhibit excellent corrosion resistance as rated according to ASTM D1654. The corrosion test results after 2,000 hours of cyclic exposure are provided in Table 1 below. The NA-PAST pretreatment yielded excellent corrosion resistance for all of the aluminum alloys tested and was found to be most effective on the 5XXX series aluminum substrate. In general, the ACP-6 waterborne primer was more effective over NA-PAST-treated substrates than the control (MIL-P-53022).

Table 1
Coating Performance Ratings for NA-PAST Treated Aluminum Samples After 2,000 hr GM Spec 9540P Cyclic Corrosion Exposure

Sample	Primer	Topcoat	Unscribed Area Failure (%)	Rating at Unscribed Area (0-10)	Average Scribe Creepage (mm)	Rating at Unscribed Area (0-10)
NAP:P-6:TC:24	ACP-6	MIL-C-46168	0	10	0	10
NAP:P-6:24	ACP-6		0	10	0	10
NAP:MP:24	MIL-P-53022		0.401	9	0.021	9
CCC:MP:TC:24	MIL-P-53022	MIL-C-46168	0.049	9	0.015	9
NAP:P-6:TC:60	ACP-6	MIL-C-46168	0.15	9	0	10
NAP:P-6:60	ACP-6		0	10	0	10
NAP:MP:60	MIL-P-53022		0.26	9	0	10
CCC:MP:TC:60	MIL-P-53022	MIL-C-46168	0	10	0	10
NAP:P-6:TC:50	ACP-6	MIL-C-46168	0	10	0	10
NAP:P-6:50	ACP-6		0	10	0	10
NAP:MP:50	MIL-P-53022		0	10	0	10
CCC:MP:TC:50	MIL-P-53022	MIL-C-46168	0	10	0	10

Coated corrosion test specimens (ten specimens per condition) were prepared from cold rolled steel Q-Panels by the optimized NA-PAST/MPD/ACP-6 process and control pretreatments and tested for corrosion resistance under cyclic exposure. The control pretreatment was a Q-panel-supplied zinc phosphate coating (ZPC). The corrosion test results, as rated according to ASTM D1654 after 200 hours of cyclic exposure are provided in Table 2. In addition, three corrosion-resistant metal alloys (titanium 6/4, 301 stainless steel, and cartridge brass) were prepared from by the optimized NA-PAST/MPD/ACP-6 process and tested for corrosion resistance under cyclic exposure. Those corrosion test results are provided in Table 3.

Table 2
Corrosion Performance Ratings for Low Carbon Steel 1010 Alloy
Pretreated by NA-PAST and Control Methods
200 hr GM Spec 9540P Cyclic Corrosion Exposure

Sample*	Primer	Unscribed Area Failure (%)	Unscribed Area Rating	Avg. Scribe Creepage (mm)	Scribed Area Rating
NAP:P-6:LCS	ACP-6	0	10	0.012 + 0.007	9
ZPC:P-6:LCS	ACP-6	0	10	0.11 + 0.02	9
NAP:MP:LCS	MIL-P-53022	0.05 + 0.09	9	0.06 + 0.02	9
ZPC:MP:LCS	MIL-P-53022	0	10	0.4 + 0.0	9

Table 3
Corrosion Performance Ratings for Assorted Alloys
Pretreated by NA-PAST Method
500 hr GM Spec 9540P Cyclic Corrosion Exposure

Sample*	Alloy	Primer	Unscribed Area Failure (%)	Unscribed Area Rating	Avg. Scribe Creepage (mm)	Scribed Area Rating
NAP:P-6:SS	Stainless steel	ACP-6	0	10	0	10
NAP:MP:Ti	Ti 6Al-4V	MIL-P-53022	0	10	0	10
NAP:P-6:Ti	Ti 6Al-4V	ACP-6	0	10	0	10
NAP:P-6:CB	Cartridge Brass	ACP-6	0	10	0	10

The corrosion resistance measured for the bare CRS substrates prepared by the optimized NA-PAST/MPD/ACP-6 process compared quite favorably with the zinc phosphate control. The most sensitivity was found for panels primed with MIL-P-53022. Zinc phosphate-coated CRS panels primed with the control primer exhibited the highest degree of blistering around the scribed areas.

Excellent corrosion prevention and primer coating adhesion maintenance was observed for the three corrosion-resistant alloys prepared by NA-PAST with both waterborne ACP-6 primer and MIL-P-53022.

4.0 CONCLUSIONS

Specifically, the NA-PAST research program resulted in the following observations and accomplishments:

- Prototype NA-PAST apparatus built and successfully tested
- Rapid paint removal and metal surface abrasion demonstrated by NA-PAST
- NA-PAST-treated aluminum specimens exhibited comparable corrosion resistance and paint adhesion to specimens treated by control methods including chromate conversion coatings after 2,000 h of cyclic corrosion test exposure (GM Spec 9540P)

Further research (not shown above) also indicates:

- NA-PAST-treated 2024-T3 aluminum specimens readily accepted a commercial electrocoat primer and the resulting panels exhibited excellent corrosion resistance and primer adhesion durability after 2,000 h of salt spray test exposure (ASTM B117).
- NA-PAST-treated 5083-H321 aluminum specimens readily accepted both powder and electrocoat primers and the resulting panels exhibited excellent corrosion resistance and primer adhesion durability after 3,500 h of salt spray test exposure (ASTM B117).
- NA-PAST-treated aluminum specimens have exhibited comparable adhesive bond mechanical properties and bond durability under hot/wet conditions to specimens treated by control processes including phosphoric acid anodizing and chromated primers with a number of different aluminum alloys.

The most effective set of blasting conditions for bonding with aluminum alloys was found to be: 40,000 psi at a stand off distance of 0.5 in with a blasting rate of 1.25 in/s. These parameters yielded the most uniformly abraded surfaces without severe structural deformation. The effect of delay or out time between process steps was found to be critical for optimum bond durability. The time between waterjet abrasion and silane application was found to be the most important and should be kept as short as possible not exceeding one hour. The time between silane application and priming was found to be most important and should be kept below 24 hours at room temperature. The out time between silane cure and e-coat primer application for paint primers does not appear to be as critical. The degree of bond durability was found to be best for low copper aluminum alloys such as 5083.

L N O Q Ö × 6

@